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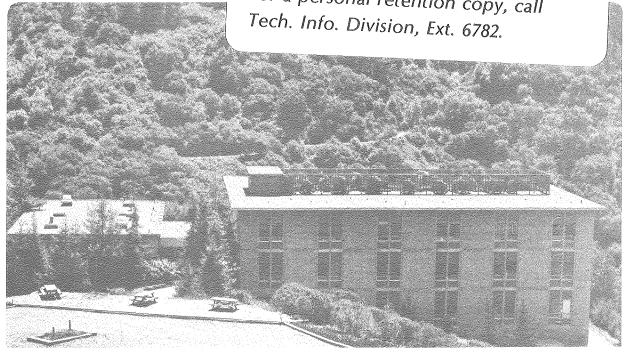
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Radiative Lifetimes of Excited Electronic States in Molecular Ions

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Abstract

Radiative lifetimes of excited electronic states of several molecular ions have been measured using a technique which permits the mass selective storage of ions for periods of many msec. This technique is used to record radiative lifetimes ranging from 60 nsec to $\sim 10~\mu \rm sec$. The use of an rf quadrupole ion trap to confine the ions reduces the problem of space charge induced spacial dissipation of ions and permits the selective excitation of electronic states. Using this technique careful measurements of the $B^2\Sigma^+_u$ state of N_2^+ and the $A^2\Pi$ states of N_2^+ and CO^+ have been made. The results obtained are in good agreement with previous studies. The analysis of the radiative lifetime for the CH^+ and CD^+ $A^1\Pi_{(v^1=0)}$ state results in a value significantly larger than earlier determinations. The new results are used to make revised estimates of interstellar abundances of CH^+ .

Introduction

The study of molecular ions in the laboratory poses special problems to the experimentalist in that large numbers of ions are difficult to work with. It is, in general, not possible to produce large numbers of a selected ion due to the usually violent nature of the ionization process which often results in molecular fragmentation as well as ionization. Rapid spacial dissipation of ions, caused by the mutual repulsion of the ions, makes it difficult to maintain significant ion densities for time periods greater than a few tens of nsecs. Particularly sensitive to this effect is the measurement of radiative lifetimes of excited electronic states of molecular ions. Many such states have radiative lifetimes in the µsec regime and the measured radiative lifetime can be severely distorted by spacial dissipation of the ions.

The study of fragment ions, in particular, presents one of the greatest challenges to the experimentalist in that they are difficult to create and, when produced, typically constitute only a few percent of the total ionic species present. The CH⁺ radical has been the subject of numerous experimental and theoretical studies. This small ion is of great importance in atmospheric chemistry and is believed to play a fundamental role in the production of many important molecular species within the interstellar clouds. Klemperer and Solomon (1972) have reported a detailed analysis of interstellar processes involving CH⁺ which are believed to have significant impact upon the molecular composition of the interstellar clouds. This ion is believed to be the precursor of CO, CN and several other molecular species. The chemistry involved in these processes is intimately related to the relative concentrations of the species involved. These concentrations must be inferred from the analysis of observed line strengths and known

or calculated oscillator strengths. For CH a large uncertainty has existed in the radiative lifetime of the $A^1\Pi$ state. Since the $A^1\Pi$ - $X^{1}\Sigma^{+}$ transition has been used to monitor interstellar CH⁺ this uncertainty manifests itself in a large uncertainty in stellar abundance and, in turn, leads to great confusion over the relative importance of certain molecular species in the interstellar medium. This uncertainty is not due to the lack of theoretical and experimental study, but to the inconsistent nature of the results. Until recently (Grieman et al., 1980), the only experimental method which had proven useful in the high resolution study of electronic transitions of molecular fragment ions was emission spectroscopy. Radiative decay rates obtained with this technique are subject to errors which are often difficult to identify or estimate. The cascading of population from highly excited electronic states and the rapid spacial dissipation of ions due to electrostatic repulsion can lead to distortions in the observed radiative lifetime of a given electronic level.

We have developed a technique with which we obtain the laser induced fluorescence spectra of ions confined to a small (1 cc) spatial region within a three dimensional radio frequency quadrupole trap. This trap is similar to the arrangement described by Benalin and Audoin (1973), and it allows us to store large numbers of ions for time periods which are limited only by collisions with background neutral gas molecules. Using a typical Langevin estimate for the ion-neutral collision rate, we find that for a neutral gas background pressure of 10⁻⁵ Torr, each ion will experience one collision per msec. This is expected to be an upper bound for the actual collision rate and, in practice, we find little difficulty in storing reactive species, such as CH⁺, for periods of up to 10 msec in this pressure range. Because the trap can store ions

for such long periods this arrangement provides an attractive possibility for the study of radiative decay rates. Ions which are in the ground (or an optically metastable) electronic state are excited with a brief laser pulse and the resulting fluorescence monitored as a function of time. The observed decay rate provides an unambiguous measurement of the upper levels' radiative lifetime.

The experimental system described here is capable of storing ions in a mass selective mode, removing doubt, in most cases, as to the identity of the ion under investigation. The degree of mass differentiation is variable, and in the high resolution mode of operation ions differing by only 1 amu can be resolved. Such resolving power is important in any studies involving hydrogen-containing ions.

We present here results obtained using this technique for several molecular ions. The technique used in the present study has been used to measure radiative lifetimes of excited molecular ions ranging from a few tens of nsec to nearly ten usec. Lifetime results for several molecular ions which have been carefully studied in the past using unrelated techniques are in good agreement with accepted values. The result obtained for $\operatorname{CH}^+ \operatorname{A}^1 \Pi_{v=0}$, however, is significantly longer than those obtained to date by alternative methods. The result obtained here, 815 nsec, is used to make revised estimates of interstellar CH^+ abundance.

Experimental

The experimental arrangement used in this study has been described previously (Grieman et al., 1981; Mahan and O'Keefe, 1981). Briefly, the method involves the use of a 3-dimensional rf quadrupole ion trap of the type described by Benilan and Audoin (1973). The trap consists of a cylindrical center electrode and two flat end electrodes, positioned

at opposite ends of the cylinder. The two end electrodes are made of wire mesh to aid in the collection of fluorescence. The general configuration is illustrated in Fig. 1. For a given set of parameters, such as size and electrode spacing, the frequency and amplitude of the applied voltage will determine the ion mass which will be stored within the electrode structure. If a dc bias is applied to the rf voltage a variable resolution is introduced to the mass selection permitting up to unit mass resolution. Such resolution was critical in the present study which required the isolation of CH_4^+ from C^+ and CH_2^+ , all of which are formed in comparable quantities in the electron impact ionization of CH_4 .

Recent studies of atomic ions confined in a quadrupole ion trap, similar to our own, have shown the spacial distribution of ions to be nearly Gaussian with the density peaking at the trap center (Knight and Prior, 1979). These studies also revealed the ions to have a Doppler width of $\sim 1~\rm cm^{-1}$, corresponding to a translational temperature of several thousand degrees.

Ions are created by electron impact ionization of selected background neutral gas which is fed into the vacuum chamber through a variable leak valve and maintained at a pressure of from 10^{-6} to 10^{-5} Torr. The experimental timing sequence is best understood by considering one experimental cycle consisting of three main parts: ion production and confinement, laser excitation of the trapped ions, and fluorescence signal detection. The timing sequence is illustrated schematically in Fig. 2.

The experiment begins with the initiation of an electron beam which is directed into the center of the trap where they ionize background gas molecules. The duration of this electron pulse is variable and is

typically 1 to 5 msec. The electron gun is then gated off through the application of a high voltage pulse to it's primary focusing electrode. A variable delay period of from 0.1 to 1.0 msec then ensues during which trapping is allowed to stabilize and excited electronic states formed during ionization are permitted to relax radiatively. Following this delay a 10 nsec, 1 cm⁻¹ bandwidth laser pulse from a dye laser is passed through the center of the ion cloud. The dye laser is pumped by either a nitrogen laser or a Nd:YAG laser. Laser induced fluorescence is subsequently monitored at right angles to the laser beam, passing through the wire mesh end electrodes into a cooled photomultiplier tube. After the collection of fluorescence the ions are pulsed out of the trap and directed to an electron multiplier, producing a signal which is proportional to the number of ions stored in the trap. Both this signal, and a measurement of laser power, are used to normalize the intensity of the fluorescence signal. The final measurement in the cycle is a signal from an optogalvanic discharge cell which is used to calibrate the dye laser frequency as it is scanned (Ling and Schenck, 1978).

An on-line PDP-8 computer is responsible for the overall control of the experiment. Following the completion of each experimental cycle, the computer gathers each of the measured signals from the detection electronics and initiates a new cycle. After a predetermined number of cycles the computer steps the laser wavelength and begins to accumulate data at the new frequency. The computer stores the data, normalizes it and produces hard copies of the final spectrum. This procedure results in the collection of laser excitation spectra.

In the determination of radiative lifetimes, the experimental arrangement is modified somewhat. Control of the experimental timing is shifted from the computer to an internally controlled cycle. The timing

sequence is unchanged when operating in this mode, but the laser frequency remains fixed, and the signal is collected continuously. The output signal from the PMT is fed into a Tracor Northern NS575 digital signal averager with a Biomation time base.

This system provides a minimum channel width of 10 nsec which is suitable for the radiative decay rates encountered in the present studies. The signal averager is triggered by the pulse which initiates the detection gate in the normal mode of operation. The total width of the signal averager's time base is 1024 channels. In the experiments involving CH^+ , CD^+ , and the $\mathrm{N_2}^+$ B² E⁺ state, a channel width of 10 nsec was used providing a full scale of 10.24 µsec. In the experiments involving CO^+ a channel width of 20 nsec was used providing a full scale of 20.48 µsec. A channel width of 50 nsec was used to measure radiative lifetimes of the $\mathrm{N_2}^+$ A² II state, resulting in a full scale of 51.2 µsec.

For radiative decay measurements the dye laser is tuned into resonance with a strong transition in the vibronic band under study. The resulting fluorescence signal as a function of time is then accumulated in the signal averager for a period of several thousand experimental cycles. The dye laser is then detuned from resonance, typically by several A, and a background signal is subtracted for an equivalent time period. Data from the signal averager are then transferred to the PDP-8 computer for analysis. The experimental arrangement is schematically depicted in Fig. 3.

Results and Discussion

A.
$$\underline{N_2}^+$$
 and \underline{CO}^+

The isoelectronic molecular ions, N_2^+ and CO^+ , are both of great importance in interstellar as well as atmospheric chemistry. These

isoelectronic species share a common ordering of electronic states (for the lowest three levels) and so it is of interest to study both ions and to draw comparisons between them. In addition, the radiative lifetimes of excited states in these ions range from 55 nsec ($B^2\Sigma$ state of CO^+) to 10 µsec ($A^2\Pi_u$ state of N_2^+) providing convenient test points for our system's ability to accurately measure lifetimes in this range. The potential curves (for the electronic states of interest here) are reproduced in Fig. 4 for N_2^+ . The potential curves for both ions have the same general form, a low lying $^2\Pi$ state, nested deeply in the $X^2\Sigma$ well, and a $^2\Sigma$ state at higher energy.

The $B^2\Sigma - X^2\Sigma$ systems of both N_2^+ and CO^+ have been thoroughly studied in the past (Lofthus and Krupenie, 1977, and Fowler et al., 1969). The radiative lifetime of N_2^+ $B^2\Sigma_{ii}^+$ (v=0) is 60 nsec for low N levels, and the corresponding value for CO is 55 nsec. Because these lifetimes are so short they will not be significantly distorted by space charge repulsion effects. The build up of high positive ion density results in the rapid depletion of ions from the viewing region as the ion cloud expands. This effect is only important for radiative lifetimes greater than a few hundred nsec. Thus, the values measure for the $B^2\Sigma$ state of N_2^+ and CO^+ should be reasonably accurate. A test of our technique's ability to accurately measure short radiative lifetimes is presented by the study of either of these states. The $B^2 \Sigma_{11}^+ (v=0)$ level of N_2^{+} is easily accessed using our dye laser and was studied as a test case. Perturbations of the N = 40-45 levels of the N_2^+ B² Σ_u^+ (v=0), caused by the $\mathrm{N_2}^+$ $\mathrm{A^2II}$ state, have been reported to increase the radiative lifetimes of these levels by as much as 20 nsec (Dufayard et al., 1974).

Measurements of the radiative lifetime of several levels in the $B^2\Sigma_{\mathbf{u}}^+(\mathbf{v}=0)$, including some of the reportably perturbed levels, were made and the results summarize in Table I. The perturbed levels proved to have easily measurable increases in radiative lifetime, up to 17 nsec above the unperturbed value of 60 nsec, in agreement with the earlier reports. Typical results for the N = 32 level of $N_2^{+}\Sigma_{\mathbf{u}}^+(\mathbf{v}=0)$ are reproduced in Fig. 5.

To test the sensitivity of our technique in the measurement of much longer radiative lifetimes we studied several levels in the ${ t A}^2\Pi$ state of both CO^{\dagger} and N_2^{\dagger} . The variation of radiative lifetime with vibrational level in the A²II state of CO⁺ has been the subject of several experimental studies, the results of which are summarized in Table II. In contrast to the short radiative lifetimes found in the $B^2\Sigma$ state of this ion, the $A^2\Pi$ state lifetime is on the order of several usec and, hence, will be subject to large perturbations due to electrostatic repulsion if steps are not taken to confine the ions or to reduce the space charge effect. Several groups have attempted to deal with the effect of positive space charge buildup, both theoretically and experimentally (Möhlmann and DeHeer, 1976, and Curtis and Erman, 1977). The poor agreement between these studies reflects the difficulties involved in modeling the space charge effects. Because the ion trap used in the present study confines the ions to a small volume for periods of many msecs, the perturbations caused by the electrostatic repulsion of the ions can be avoided. The use of a laser to selectively excite a particular level in the upper state removes the possibility of population cascading which would result in the distortion of the decay rate through a lengthening of the observed radiative lifetime. The results obtained

here for the v' = 1,2,3, and 4 levels of $CO^+A^2\Pi$ are presented in Table II. The trends in lifetime variation with v' are in agreement with the other studies although the results we obtain are some 30% higher than those of Curtis and Erman (1977).

As noted by Holland and Maier (1972), the lifetime of an excited electronic level with vibrational quantum number v' can be expressed as

$$\tau_{\mathbf{v'}}^{-1} \approx \sum_{\mathbf{v''}} g_{\mathbf{v'},\mathbf{v''}} \bar{R}_{\mathbf{e}}^{2} \omega_{\mathbf{v'},\mathbf{v''}}^{3}, \tag{1}$$

where \bar{R}_e is the electronic transition moment. They have calculated the relative τ_{rad} 's for levels v' = 0-8 in the CO^+ $A^2\Pi$ state using the assumption of constant R_e , and have normalized these values to their measured ones. These values are presented in Table II for comparison.

The $\text{A}^2\Pi$ state of N_2^+ , with vibronic lifetimes of ~10 µsec, presents the greatest challenge to our technique. The strongest vibronic bands in the system are deep in the red (~8000 Å), which is a poor spectral region for lasers. In addition, because the transition is so weak, high laser powers are required to induce significant excitation. The (5,0) band of this system was studied and the decay rate of its laser induced fluorescence recorded. This resulted in the value of $\tau_{(\text{V'}=5)} = 9.3 \pm 1.0~\mu\text{sec}$ which is in good agreement with the results of Holland and Maier (1972), and of Peterson and Moseley (1973).

B. CH and CD+

The technique discussed here may prove to be most useful in the study of fragment ions; particularly those fragment ions which are produced only in small quantities. Ion densities achieved using this technique are limited only by fixed experimental parameters and thus, in principle, comparable densities of any chosen ion may be attained.

We have recently used this technique to study the $A^1\Pi - X^1\Sigma^+$ system of both CH^+ and CD^+ (Grieman et al., 1981a). The collision free environment of our low pressure ion trap preserved the initial rotational-vibrational distribution of the fragment which resulted in the observation of many previously unobserved rotational levels. This permitted a reanalysis of molecular constants resulting in more accurate constants for the (0,0) band of CH^+ and the (0,0) and (2,1) bands of CD^+ . A segment of the CD^+ $A^1\Pi + X^1\Sigma^+$ (0,0) band is reproduced in Fig. 6.

The radiative lifetime of the $A^1\Pi$ (v'=0) state of CH^+ has been the subject of numerous studies due to its great importance in the chemistry of interstellar clouds. Early studies resulted in radiative lifetimes which were ~70 nsec (Smith, 1971; Anderson et al., 1973). Subsequent investigations pushed the value up to several hundred nsec (Brzozowski et al., 1974; Brooks and Smith, 1975). Recent studies by Erman (1977) in which attempts were made to neutralize space charge effects resulted in a radiative lifetime for the $A^1\Pi_{(v'=0)}$ state of 630 nsec. Some of these studies suffer from poor spectral resolution and, in several cases, have likely been distorted due to the presence of overpowering impurity Those studies which resolve specific rotational components of the transition are still subject to a large distortion due to electrostatic repulsion. The effect can be quite large for fragment ions, such as CH+, since the fragment is typically formed in small quantities $(\mathrm{CH}^+ \simeq 3\% \mathrm{\ of\ total\ ionization\ from\ CH}_\Delta)$ and high ion densities must be formed to produce a measurable signal. These high ion densities result in large space charge effects.

Relatively high densities of CH $^+$ ions can be generated in our trap ($\geq 10^6/\text{cc}$) and, as in the previously discussed studies, the effects of space charge repulsion are avoided. We have carried out studies of the

decay rate of the $A^1\pi(v'=0)$ state of both CH⁺ and CD⁺. In each case the (0,0) R branch bandheads were excited and total fluorescence monitored as a function of time. The results are tabulated in Table III. The result obtained for CH⁺ $A^1\pi(v'=0)$, 815 nsec (Fig. 7), is some 30% higher than the closest previously determined value. This value, 630 nsec, was arrived at using the modified high frequency deflection (HFD) technique developed by Erman (1975) in which low energy electrons are injected into the ionization region to reduce the space charge generated by the positive ions. This technique has considerably reduced the effect of electrostatic repulsion, however, the actual extent of the effect's reduction is not well documented. Even with the space charge neutralization this technique results in a radiative lifetime for the CO⁺ $A^2\pi(v'=0)$ state of 2.85 µsec which is more than 1.0 µsec lower than the presently determined value of $\tau_{v'=0}$ = 3.96 µsec.

Examination of the results tabulated in Table II reveals rather good agreement between the values of $\tau_{\rm rad}$ obtained by Möhlmann and DeHeer (1976), Holland and Maier (1972) and those obtained in the present study. These studies were all made under low collision conditions $(10^{-5}-10^{-2}~{\rm Torr})$. The results obtained by Bondybey and Miller (1978) were obtained in a high pressure study (~1.0 Torr) and thus involve the extrapolation of measured valves back to zero pressure. If the radiative lifetimes of the CO⁺ $\Lambda^1 \Pi(v'=0)$ state obtained in the low pressure experiments are averaged together the result is $\tau_{(v'=0)} = 3.88$ µsec. If a correction factor, based upon the ratio of this average value for the CO⁺ $\Lambda^2 \Pi(v'=0)$ radiative lifetime to the value measured using the HFD technique, is applied to the HFD result for CH⁺ $\Lambda^1 \Pi(v'=0)$, the result,

$$\tau = \frac{3.88}{2.85} \cdot 630 \text{ nsec} = 858 \text{ nsec},$$
 (2)

is in excellent agreement with the result obtained using the technique described here.

If the oscillator strength of the CH⁺ $A^1\Pi - X^1\Sigma^+$ (0,0) band, as determined by Erman (1977), $f_{0,0} = 7.2 \times 10^{-3}$, is scaled by the ratio of the radiative lifetime determined using the HFD technique to that determined here, the result is

$$f_{0,0} = \frac{630}{815} \cdot (7.2 \times 10^{-3}) = 5.57 \times 10^{-3}.$$
 (3)

This result is within $\sim 15\%$ of the $f_{0,0}$ calculated by Yoshimine <u>et al</u>. (1973).

The oscillator strengths of molecular transitions can be used to make estimates of column densities and relative abundances of molecules and ions in the interstellar medium. Because CH and CH⁺ are believed to be so important in the formation of many interstellar molecules, the correct modeling of their formation and chemistry is of fundamental significance. Any theory dealing with the formation of CH and CH⁺ must accurately account for the observed abundances of these species to be acceptable. Thus, it is imperative to obtain precise determinations of the actual abundances of these molecular species through independent means. Recent measurements of CH⁺ column density (Vanden Bout and Snall, 1980) used an $f_{0,0}$ value of .014, based upon the studies of Brooks and Smith (1975). Using the revised value of $f_{0,0}$ as determined in the present study the revised column densities are N = 2.8 x 10^{13} , 4.0×10^{13} , and 3.0×10^{13} cm⁻² toward 20 Tau, ξ Per, and ξ Oph, respectively.

Conclusions

The experimental technique described here has been used to measure radiative lifetimes of molecular ions which are as short as a few tens of nsec, and as long as ~10 µsec. The use of mass selection allows the unambiguous assignment of fluorescence signal to a particular ion, and the use of selected laser excitation of specific states avoids the problem of population cascading. The rapid spacial dissipation of ions, due to electrostatic repulsion, is avoided in the present study through the use of an ion trap within which large densities of selected ions ($\geq 10^6$ ions/cc) can be maintained for periods of many msec. Using this technique we have made careful measurements of the $A^1\Pi_{(v'=0)}$ radiative lifetime for both CH^+ and CD^+ . The results agree reasonably well with the <u>ab initio</u> calculations of Yoshimine, et al. (1973). A revised estimate of the oscillator strength of the CH^+ , $A^1\Pi_- X^1\Sigma_+$ system is used to predict a nearly threefold increase in interstellar CH^+ densities over earlier estimates (Vanden Bout and Snell 1980).

Acknowledgments

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Table I. Measured radiative lifetimes for selected rotational levels of ${}^{+}_{2}{}^{B}{}^{2}{}^{+}_{u}(v'=0)$

N,	Lifetime	(nsec)
10	62	
30	58	
32	60	
42	79	
43	77	

Table II. Measured radiative lifetimes (in μsec) of the CO⁺ $A^2\Pi$ state for v^* = 0-4

V	A	В	C	D	measured E	calc
0	calc(3.96) ^a	3.82(<u>+</u> 0.19)	2.85(<u>+</u> 0.2)	4.6(+0.5)		3.85
1	3.51(±0.1)	3.58(±0.18)		3.8(±0.5)	3.49(±0.24)	3.41
2	3.25(+0.1)	3.09(±0.15)		3.1(±0.7)		3.09
3.	2.90(+0.1)	2.85(±0.14)			2.78(±0.19)	2.84
4	2.60(+0.15)	2.69(±0.13)			2.63(±0.18)	2.66

a This valve is calculated by scaling our measured valve for $\tau_{v'=0}$ by the ratio of $\tau_{v'=0}$ to $\tau_{v'=1}$ calculated by Holland and Maier (1972).

Explanation of Table Headings

A. Results of the present study; B. Results of Möhlmann and DeHeer (1976); C. Result (for v'=0) of Curtis and Erman (1977); D. Results of study by Bondybey and Miller (1978); E. Measured and calculated results of Holland and Maier (1972). The calculations are based upon the assumption of constant \bar{R}_{ρ} .

Table III. Measured radiative lifetimes for the CH and CD A $^{1}\Pi_{\left(v^{\,i}=0\right)}$ state

		Lifetime (nsec)			
	A	В	C		
CH ⁺	815 (+25)	630 (<u>+</u> 50)	250		
CD ⁺	820(±50)				

Explanation of columns: A. results obtained using laser excitation of trapped ions (present study). B. Results obtained using space charge neutralization technique (Erman 1977). C. Results obtained using electron beam phase shift technique (Brooks and Smith, 1975).

Figure Captions

- Fig. 1 Schematic representation depicting a vertical slice of the quadrupole ion trap used in this study. A radio frequency voltage is applied to the center ring electrode while the top and bottom electrodes are maintained at ground potential. Ions, spacially confined to the enclosed region, possess a nearly Gaussian density distribution peaking at the center of the trap.
- Fig. 2 Schematic representation of the timing sequence of an experimental cycle.
- Fig. 3 Diagram depicting the experimental arrangement used for the measurement of radiative lifetimes.
- Fig. 4 Potential energy curves for several electronic levels of N_2 and N_2^+ . A similar ordering of electronic states is found for CO^+ .
- Fig. 5 Decay rate of electronically excited N_2^+ . The laser excitation of the $B^2\Sigma_{\mathbf{u}(\mathbf{v'=0})}^+$, N'=32 yielded the data shown here. A least squares fit to the data resulted in a value of 60 nsec for the radiative lifetime of this level.
- Fig. 6 Portion of the LIF spectra obtained for the ${\rm CD}^+$ ${\rm A}^1\Pi$ ${\rm X}^1\Sigma^+$ (0,0) band. Several members of the (2,1) band can also be seen. The P₁₀ line of the (2,1) band, which is obscured by the stronger (0,0) band is denoted by an X.
- Fig. 7 Radiative decay rate of the $A^{1}\Pi_{(v)=0)}$ J=3 level of CH⁺.

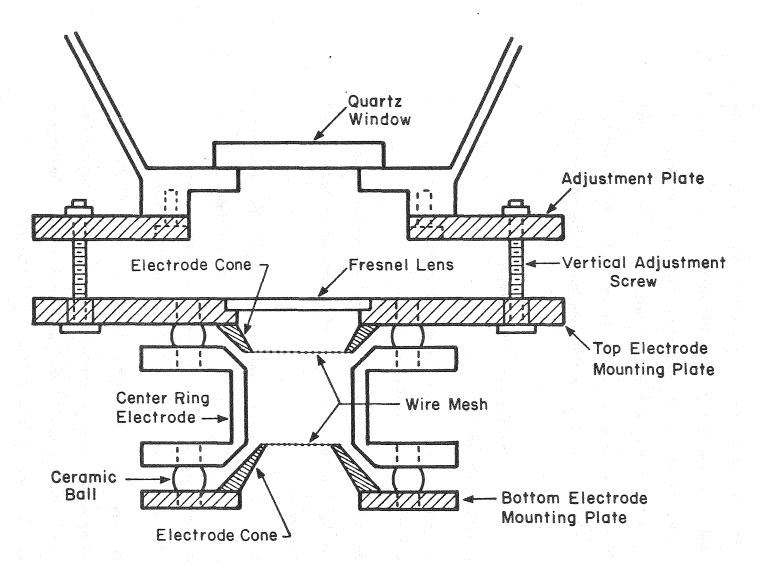
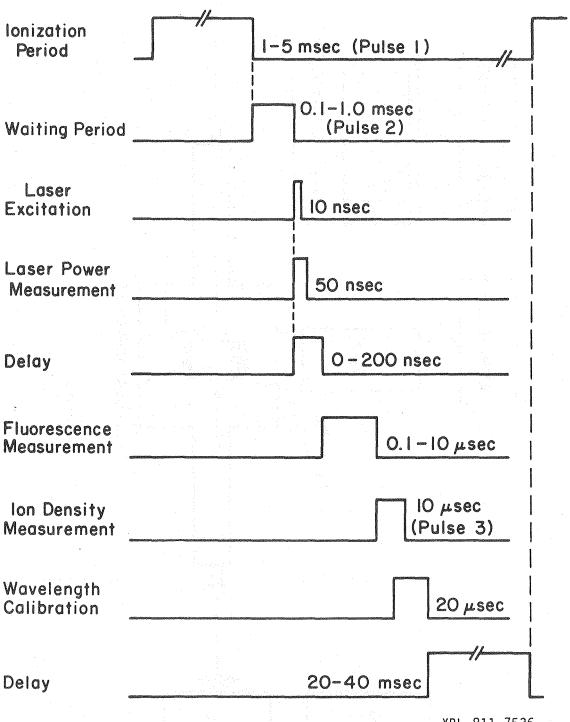


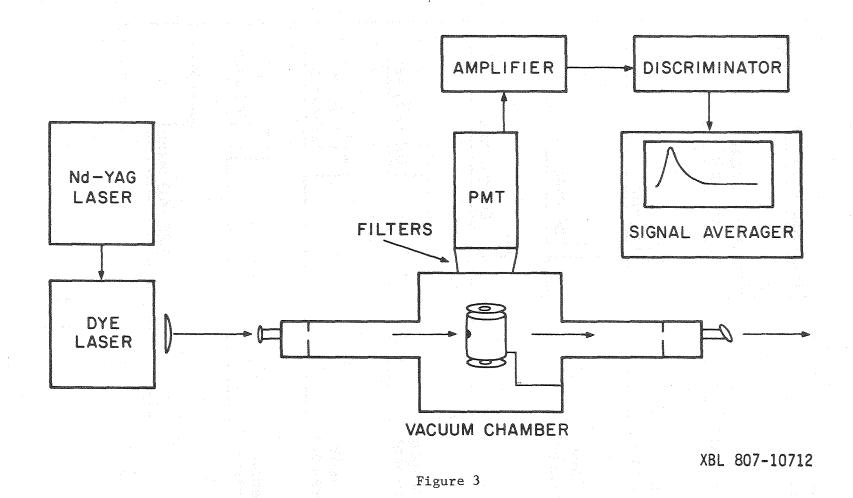
Figure 1

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XBL 811-7536

Figure 2



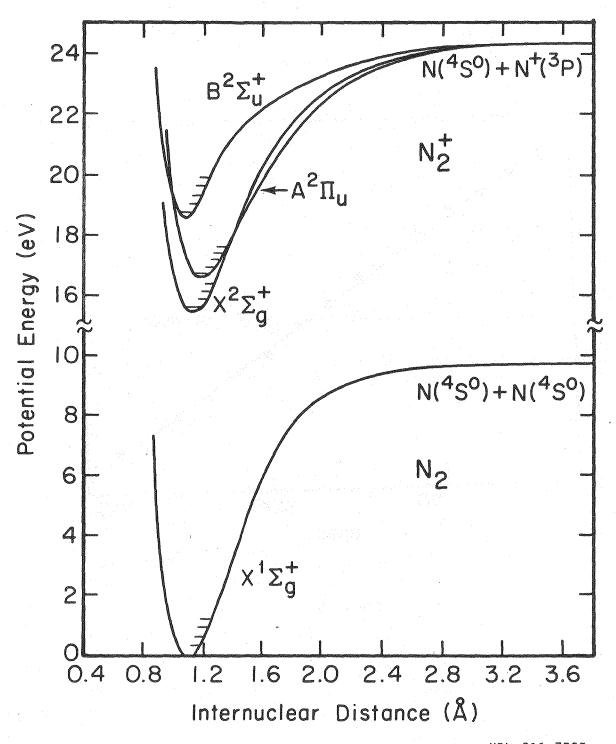


Figure 4

XBL 811-7535

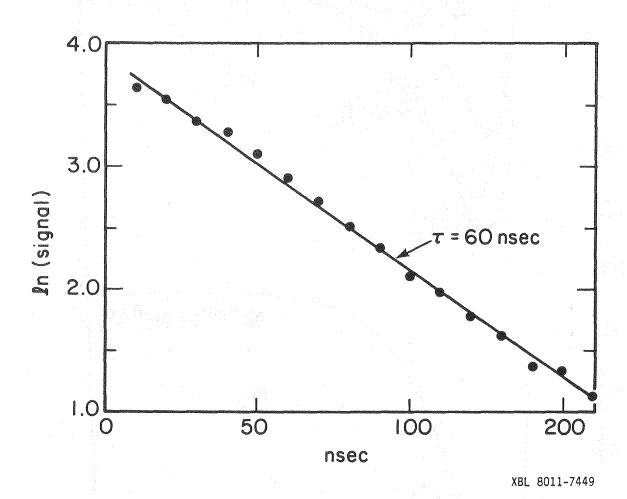


Figure 5

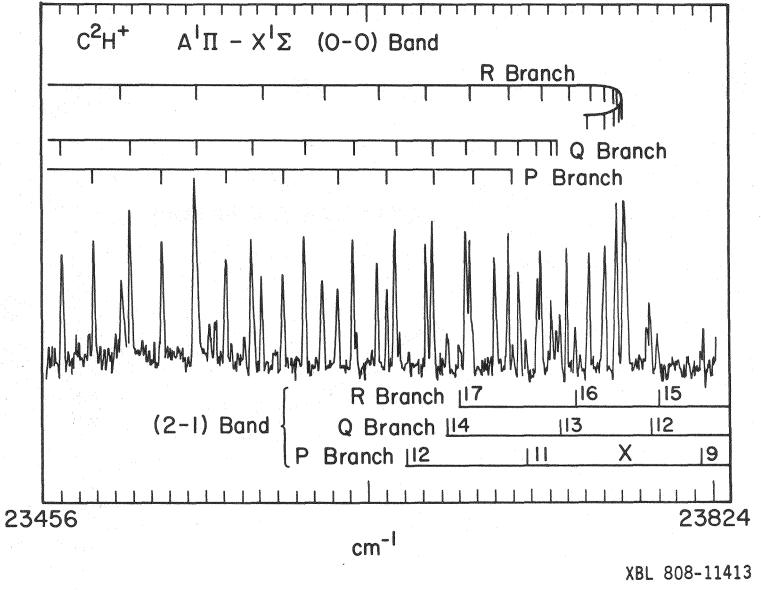


Figure 6

